Room Temperature Selective Epoxidation of Cyclooctene Over Ag nanoparticles Supported on Tungsten Oxide with H_2O_2

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Abstract: We have prepared silver nanoparticles (AgNPs) supported on tungsten oxide (WO_3) in presence of cetyltrimethyl ammonium bromide (CTAB), a catinic surfactant. The catalyst was characterized by XRD, ICP-AES, FT-IR, SEM and TEM. The catalyst was highly active for selective oxidation of cyclooctene to cyclooctene oxide at room temperature with H_2O_2. The reusability of the catalyst which is a prerequisite for practical applications was performed and it was found that the catalyst exhibits no significant changes in its catalytic activity even after three reuses. A cyclooctene conversion of 55% with cyclooctene oxide selectivity of ~99% was achieved over this catalyst

Keywords: Ag nanoparticles, Tungsten (VI) oxide, Cyclooctene, Cyclooctene oxide, H_2O_2, Selective epoxidation.

INTRODUCTION

Epoxidation is an important chemical reaction in organic synthesis since the epoxides are valuable chemical intermediates as they undergo a large range of reactions [1, 2]. So catalytic epoxidation of olefins affords considerable academic and industrial interest. Epoxidation of alkenes through the electrophilic addition of oxygen to carbon-carbon double bond remains one of the most significant challenges in chemistry. Various transition-metal catalysts have been reported to catalyze alkene epoxidation reactions, but the processes are mostly homogeneous in nature and also suffers from separation and recycling [3-8]. Epoxidation of substituted alkenes successfully achieved by using stoitiometric amounts of peracids such as peracetic acid and m-chloro benzoic acid [9]. However, the use of peracids is not environmentally benign process as equivalent amounts of acid waste are produced [10]. There have been several reports for alkene epoxidation through immobilization of homogeneous catalysts, but often leaching of the active species and poor thermal stability hinder the overall process [11]. There is a strong need for the development of new epoxidation processes which employ safer oxidants and little waste. Catalytic epoxidation of alkenes with hydrogen peroxide is of high importance because of the sustainable nature of the reaction since hydrogen peroxide has the high content of active oxygen species (47 wt %) as it generates water as the sole byproduct [12]. Moreover, H_2O_2 is cheaper and safer to use than the other peroxides and peracids. Tungsten-based catalysts, polyoxometalates, supported tungsten oxides are effective catalysts for epoxidation [13-16]. Selective oxidation by tungsten-based catalysts with H_2O_2 has been widely investigated because of their high reactivity for oxidation as well as an inherent poor activety for the decomposition of H_2O_2. But often the use of an excess of H_2O_2 with respect to the substrates, requirement of microwave irradiation or additives are the major setbacks of those processes [17-20]. Therefore, the exploration of a true heterogeneous, efficient tungsten-based catalyst with ease of separability and recyclability for green oxidation with H_2O_2 applicable to a wide range of substrates is still highly demanding. The production of cyclooctene to cyclooctene oxide is of great importance, since cyclooctene oxide is an important chemical intermediate for the production of various oxygenated products like cyclooctane diol, cyclooctenone etc.

Herein, we report the fabrication silver nanoparticles anchored on tungsten oxide which displayed excellent properties as heterogeneous catalyst for liquid phase selective oxidation of cyclooctene to cyclooctene oxide using hydrogen peroxide as an environmentally benign oxidant at room temperature. The catalyst showed 55% cyclooctene conversion with cyclooctene oxide selectivity of 99%. The practical importance is the finding of excellent activity towards formation of cyclooctene oxide and the ability to recover and reuse the catalyst with no significant loss in catalytic activity. The newly developed Ag/WO_3 nanostructure catalyst with excellent activity may help further to design new catalyst with enhanced activity toward other oxidation reactions.

EXPERIMENTAL

Materials

Hydrogen Peroxide (50 wt % in water) was purchased from Merck KGaA, Darmstadt, Germany.

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$AgNO_3$, H_2WO_4, cetyltrimethylammonium bromide, hydrazine hydrate, ammonium hydroxide, cyclooctene (purity > 99.9%), acetonitrile (HPLC grade) were purchased from Sigma-Aldrich Co. All the chemicals were used without further purification.

Catalyst Preparation

The Ag/WO_3 catalyst was prepared by modifying our own preparation method [7]. In a typical preparation method, tungstic acid and silver nitrate at a desired molar ratio (taking 4% Ag loading on WO_3 by weight) were dissolved in water. The pH of the medium was made 9, by gradual addition of NH_4OH solution drop wise. Then CTAB solution was poured in the solution followed by the addition of 0.5 g of NaCl dropwise. The resultant mixture was stirred for 3 hours. A solution of hydrazine monohydrate (80% aqueous solution), was added drop wise to the well stirred mixture. All the reagents were used maintaining the ratio: Ag: CTAB: hydrazine: H_2O = 1: 0.30: 1: 400. The total solution was stirred for another 30 minutes and then transferred to 100 °C autoclave for 24 hours. After that, the so-obtained product was washed with ethanol and dried in 80 °C oven for 6 h, followed by calcination at 550°C for 6 h in nitrogen.

Characterization Techniques

Powder X-ray diffraction spectra were collected on a Bruker D8 advance X-ray diffractometer fitted with a Lynx eye high-speed strip detector and a Cu K_α radiation source with a wavelength of 1.5418 Å. Diffraction patterns in the 2°–80° region were recorded at a rate of 0.5 degrees (2θ) per minute. The resulting XRD profiles were analyzed to identify the crystal phase of the compound using reference standards. The line width of the most intense XRD peak was taken for estimation of crystallite size by the Scherrer equation.Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanumhexaboride (LaB_6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were analyzed by spreading them on a carbon tape. Energy dispersive X-ray spectroscopy (EDX) was used in connection with SEM for the elemental analysis. The elemental mapping was also collected with the same spectrophotometer.Transmission electron microscopy (TEM) images were collected using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. The particle size and distribution of the samples were analyzed by TEM. Chemical analyses of the metallic constituents were carried out by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES); model: PS 3000 uv, (DRE), Leeman Labs, Inc, (USA). To determine the metal loading of the catalyst, the Ag/WO_3 sample was at first dissolved in a solution containing 2 (M) NaOH and 3% H_2O_2 solution to dissolve the tungsten part, here silver part remains as residue. After filtration, the residual part was treated with conc. HNO_3 and 3% H_2O_2 to dissolve silver. Thereafter, both the silver and tungsten containing solution was analyzed through ICP-AES.

Liquid Phase Hydroxylation

Liquid phase oxidation of cyclooctene was carried out in a double neck round bottom flask at room temperature in an oil bath connected with a spiral condenser using 0.10 g catalyst, 10 ml acetonitrile solvent and 1 g of cyclooctene to which 1.85 g H_2O_2 (50% aq. solution) was added dropwise. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis. At the end of the reaction, the solid particles (catalyst) were separated by filtering during the hot condition and products were analysed by gas chromatograph (GC, Agilent 7890) connected with a HP-5 capillary column (30 m length, 0.28 mm id and 0.25 µm film thickness) and a flame ionization detector (FID). The C- balance as well as material balance was carried out for most of the experiments and it was found between 98-102%. For the reusability test, after completion of the reaction, the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with acetone and reused as such for multiple circles.

RESULTS & DISCUSSION

Catalyst Characterization

The powder XRD pattern of the catalyst in Figure **1** showed the peaks at 2θ values of 23.2º, 23.5º, 24.3º, 33.2º and 34.2º (2θ), which corresponds to the monoclinic WO_3 (JCPDS No. 43-1035). In addition, the four diffraction peaks at 2θ values of 38.1, 44.3, 64.4 and 77.4° corresponding to the metallic Ag crystal faces of (111), (200), (220)and (311) respectively, (JCPDS No. 04-0783).The metallic phase of silver does not change after the reaction which is also confirmed by XRD analysis (Figure **1e**). The amount of silver present in the Ag/WO_3 nanostructure catalyst was estimated by ICP-AES. SEM images showed the samples

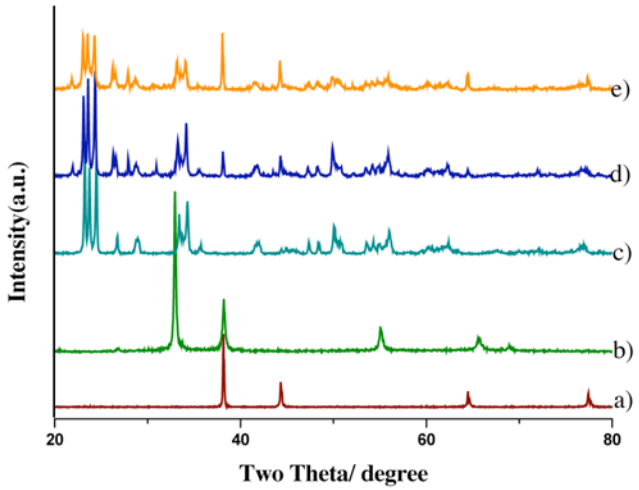

Figure 1: XRD patterns of **a)** Ag (0), **b)** Ag (I) oxide, **c)** W(VI) Oxide, **d)** prepared Ag/WO_3 catalyst **e)** spent Ag/WO_3.

prepared by our own surfactant-assisted procedure exhibit nearly uniform rod-like structure with diameter around 80 nm (Figure **2a**). EDS showed only the presence of silver, oxygen and tungsten and no other impurities were observed in the EDS spectra (Figure **2b**). Transmission electron microscopy (TEM) revealed a one-dimensional rod-like morphology of tungsten oxide (Figure **3a**) with an average width of ~80 nm deposited by silver nanoparticles. The spacing of the lattice fringes were found to be about 0.38 nm and 0.20 nm, which are attributed to the (002) plane of WO_3 and (200) plane of metallic Ag, respectively (Inset, Figure **3a**). The TEM measurements of the reused catalyst (Figure **3b**) showed that average sizes of the silver nanoparticles are in the same range after the reaction. So we can say that the catalyst is stable and reusable. So the sintering and agglomeration of silver nanoparticles during catalysis can be ruled out. The embedment of the surfactant cetyltrimethyl ammonium bromide (CTAB) with the $Ag\text{-}WO_3$ moiety was confirmed by the FT-IR analysis of the Ag/WO_3 catalyst as shown in Figure **4.** Before calcinations, the sample showed the presence of organic moiety in the catalyst which suggests the embedment of surfactant CTAB with the catalyst. The peak at 1424 cm^{-1} corresponds to the symmetric stretching vibration of $CH_3\text{-}N^+$ moiety of CTAB. The frequency between 1600 and 3000 cm^{-1} may be due to the CH_2 symmetric antisymmetric vibrations region [21]. However, after calcinations, the absence of organic moiety reflects the complete removal of CTAB during calcinations (Figure **4b**). The morphology of the catalyst is not affected by the removal of surfactant during calcinations, thus showed the excellent stability of our prepared Ag/WO_3 nanostructure catalyst.

Activities of the Catalysts

Table **1** showed the activities of the different Ag/WO_3 catalysts in the selective oxidation of cyclooctene in liquid phase using H_2O_2 as oxidant. The Ag/WO_3 nanostructure catalyst showed 55% cyclooctene conversion with ~99% cyclooctene oxide selectivity (Table **1**, entry 4) at room temperature after 12 hours of reaction. At initial phase of the reaction, the conversion was low, but during the course of time the conversion increases keeping the cyclooctene oxide selectivity intact ~99%. We observed that with increasing Ag loading, the selectivity towards cyclooctene oxide decreased due to the formation of cyclooctenone. It has to be noted that Ag/WO_3 catalyst prepared by the conventional impregnation method

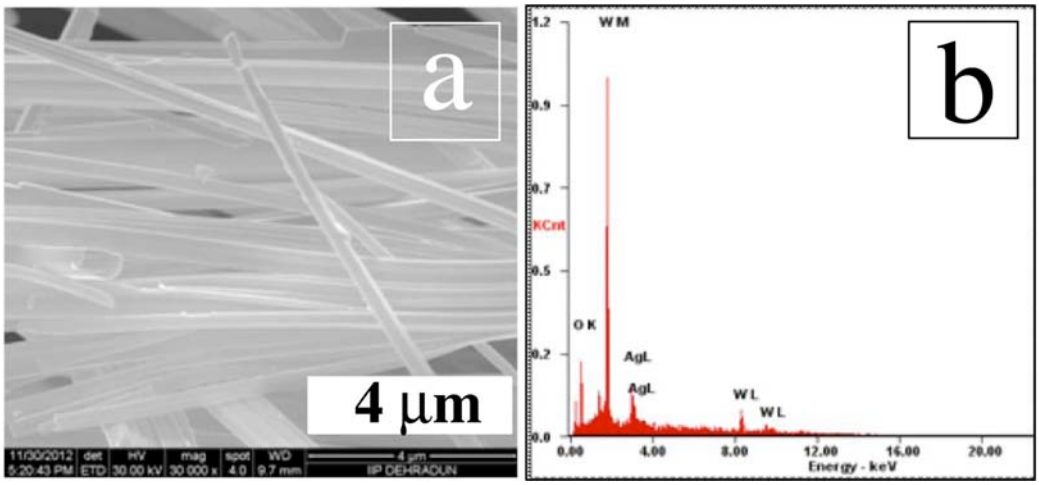

Figure 2: (a) SEM image and **(b)** SEM-EDAX image of Ag/WO3 catalyst.

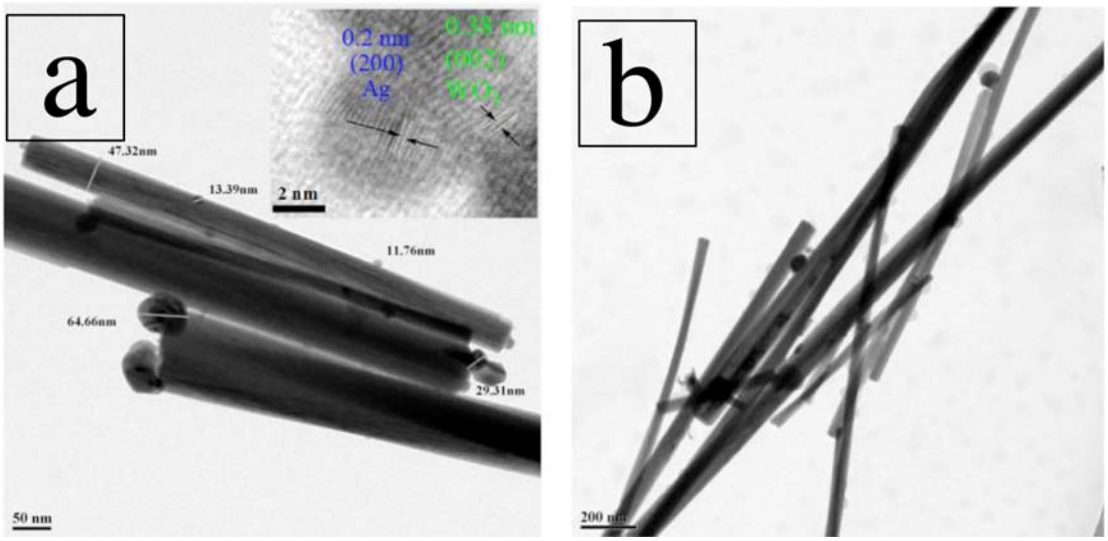

Figure.3: (a) TEM image of the fresh catalyst, inset lattice fringes, and **(b)** TEM image of the spent (after3 recycles) Ag/WO_3 catalyst.

exhibited much lesser activity due to excessive leaching of the metals (Table **1**, entry 3). Blank experiment (Table **1**, entry 6, without any catalyst) gave no conversion. This reflects the necessity of the catalyst in the reaction medium to promote the reaction. Even commercial silver or tungsten oxide alone showed very little activity (Table **1**, entry 1, 2) which confirms the cooperativity effect of the Ag/WO_3 nanostructure catalyst. The details mechanistic path is under study. Primarily we believe that the reaction occurs through the formation of tungsten peroxo species which donates electrophilic oxygen to the C=C of cyclooctene and forms cyclooctene oxide. Ag nanoparticles are supposeed to stabilize the alkene bound peroxo tungsten intermediate [22].

Reusability of the Catalyst

To check whether the catalyst is truly heterogeneous or not, the catalytic oxidation of cyclooctene was carried out with the reused catalyst under the same reaction condition. Activity of the recovered catalyst after 3 consecutive runs did not lead to any significant decline in its catalytic activity in terms of conversion and selectivity. The reasons may be attributed to mechanical loss of catalyst due to handling loses of the catalyst during filtration and drying, during regeneration. After completion of reaction, the solid catalyst was removed from the reaction mixture by filtration during hot condition and the reaction was allowed to proceed with the filtrate under the same

Table 1: Reaction Conditions of Catalytic Oxidation of Cyclooctene[a]

Entry	Catalyst	Ag Loading(%)[b]	Cyclooctene Conversion (%)[c]	Selectivity (%)[d]		H_2O_2 selectivity (%)
				Cyclooctene Oxide	Others	
1	Ag^{Com}	-	3.5	14	86	14
2	WO_3^{Com}	-	8	65	35	65
3[e]	Ag/WO_3^{imp}	3.5	12	77	23	77.06
4[f]	Ag/WO_3	3.3	55	>99	-	99
5[g]	Ag/WO_3	3.3	53	97	3	97
6	No Catalyst	-	-	-	-	

[a]Typical reaction conditions: substrate (cyclooctene) = 1g, catalyst= 0.1g, cyclooctene: H_2O_2 (molar ratio) = 1:3, reaction temperature = 35°C, time = 12 h. [b]Loading of Ag determined from ICP-AES. [c]Conversion of cyclooctene based upon the FID-GC using chloroform as external standard = [Moles of cyclooctene reacted/initial moles of cyclooctene used] x 100. [d]Selectivity = [Moles of products produced/ moles of cyclooctene reacted] x 100; [e]Ag/WO_3 catalyst prepared by impregnation method. [f]Fresh catalyst; and [g]Spent catalyst (after 3 recycles), other product includes cyclooctenone.Selectivity based on H_2O_2= [Moles of H_2O_2 required for cyclooctene oxide formation/ total moles of H_2O_2 consumed] x 100.

conditions. The reaction was completely stopped after the removal of the catalyst. Leaching test was performed for Ag and W by ICP-AES analysis using the filtrate and it was found that no Ag or W ions were present in the filtrate. We also observed that the amount of Ag and W present in the spent catalyst after three reuses is same with that of the fresh catalyst as estimated by ICP-AES. So the catalyst is truly heterogeneous in nature.

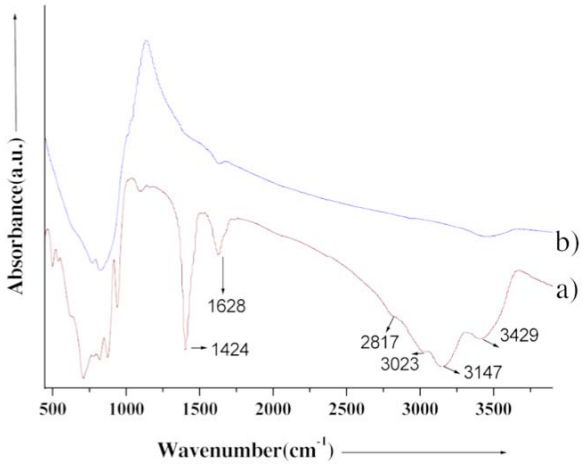

Figure 4: FT-IR of the **a)** uncalcined Ag/WO_3 catalyst and **b)** calcined Ag/WO_3 catalyst.

CONCLUSIONS

We have described the synthesis of silver nanoparticles supported on WO_3 support for the direct conversion of cyclooctene to cyclooctene oxide with hydrogen peroxide as an oxidant. The catalyst shows a cyclooctene conversion of 55% with 99% cyclooctene oxide selectivity after 12 h. The catalyst was characterized by XRD, ICP-AES, FT-IR, SEM and TEM. Furthermore, the small size of the silver nanoparticles on WO_3 support also helps preventing leaching of the active metal during the reaction, therefore, also represents as a stable and effective catalyst in terms of catalytic applications and recyclability. The catalyst did not show any leaching after three reuses, confirming the true heterogeneity of the catalyst.

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